

## DUAL MODE SORPTION AND COAL MICROPOROSITY

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### INTRODUCTION

Pyridine is one of the most effective and commonly-employed solvents for investigating coal structure. We have recently determined sorption isotherms for several coal-pyridine systems<sup>1</sup>. The most striking characteristic of these isotherms are their high linearity over a very wide pressure range. The curves also have nonzero intercepts. We propose that these isotherms can be modelled by a dual-mode sorption mechanism which has been widely used to interpret the sorption isotherms of glassy polymers.<sup>2-6</sup>

In this model, the sorption mechanism is described in terms of one population of ordinarily dissolved sorbate which resides in the coal matrix and is described by Henry's law (i.e. sorption is linear with pressure) while the second population of sorbate is considered to occupy unrelaxed free volume (micropores) within the coal matrix and is described by a Langmuir isotherm. We propose that the linear portion of the pyridine isotherms presented in this paper represent dissolution of pyridine and that the intercepts are a measure of the coal's microporosity available to pyridine. We present results on the Argonne premium Illinois No. 6 coal, including the whole coal, pyridine extract, extraction residue, and some O-alkylated coals, to support our hypothesis.

### Porosity of Coals.

The pores in porous solids are generally classified into three regimes<sup>7</sup>; macropores with diameters greater than 500 Å, mesopores with diameters from 20-500 Å, and micropores with diameters less than 20 Å. This classification is not arbitrary and is based on the characteristics adsorption effects as manifested in the sorption isotherm. In the macropore range, the pores are so wide that it is virtually impossible to map out the isotherm in detail because the relative pressures of the adsorbate (adsorbed gas) is so close to unity. In mesopores, capillary condensation takes place, usually at moderate relative pressures (greater than 0.3 relative pressure). In micropores, which are of molecular dimensions, an enhancement of the interaction potential takes place between the sorbent and adsorbate. The upper limit of size at which a pore begins to function as a micropore depends on the diameter of the adsorbate molecule; for slit like pores this limit is about 1.5 but for cylindrical pores it lies at a pore diameter of about 2.5 . As a consequence of this enhanced interaction potential, the micropore will be completely filled at low relative pressures, frequently less than 0.01 relative pressure. This paper is concerned with the micropores of coal and this low pressure region where micropores are being filled.

## EXPERIMENTAL

### Sample Preparation

Argonne Premium coals were obtained in ampoules of five grams of - 100 mesh. The coals were first dried under vacuum at 105°C to constant weight and then analyzed for carbon, hydrogen and nitrogen.

Approximately 4.5 g of the sample was Soxhlet-extracted with dry pyridine under argon for several days until the siphon liquid was clear. The pyridine solution was then filtered through a 0.4 m nylon membrane filter to insure removal of particulates and colloidal material. The filter did not plug. Most of the pyridine was removed by rotovaporization under reduced pressure at 70-80°C. Approximately 200 mL of a methanol/water (80/20 vol) mixture and 2 mL of conc. HCl were added to the flask and the mixture was stirred under nitrogen for two days. This treatment was used to remove residual pyridine. The solid extract was then filtered and dried under vacuum at 105°C for 24 h. The extractability was 27.2% (wt) for Illinois No. 6 coal. The extract were analyzed for carbon, hydrogen and nitrogen.

Most of the pyridine was removed from the extraction residues under vacuum. The residues were then treated with HCl/methanol/water and dried in a similar manner as the extracts.

### O-alkylation Procedure.

The procedure for O-alkylation of the Illinois No. 6 coal was conducted according to Liotta's method.<sup>5</sup>

### Sorption Experiments

Sorption experiments on 50 mg samples of the coals were carried out using a quartz spring balance shown in Figure 1. The balance consists of a quartz spring, a 5 L flask, vacuum inlet system, and MKS pressure transducer (0-1000 torr, 0.5% accuracy). The entire balance, including transducer, is housed in a Precision Scientific circulating (forced air) drying oven. The temperature is controlled by a I<sup>2</sup>R temperature regulator, which activates a light bulb.

The sample is suspended from the quartz spring and, as the sample sorbs solvent, the spring extends until equilibrium is reached. The extension of the spring is measured by an Eberbach cathetometer (travelling telescope). The spring is calibrated at the appropriate temperature using standard weights. The balance thus allows determination of the mass of solvent sorbed by the sample at a given partial pressure and temperature. The purpose of the 5 L flask is to minimize pressure changes caused by sorption of solvent by the sample. Quartz springs of the type used here have a linear-extension versus suspended weight relationship and exhibit no hysteresis within the range of weights for which the spring is designed.

## RESULTS

The whole coals, extracts, and extraction residues were exposed to pyridine at various vapor pressures at 50°C. Several incremental sorption experiments were conducted in that, once equilibrium was attained at a particular pressure, the pressure was raised and the system was again allowed to attain equilibrium. Generally one to two days were required for each coal-pyridine system to reach equilibrium at a given pressure. The O-alkylated systems reached equilibrium much faster, typically in less than one hour for the O-butylated and O-

octylated coals at each pressure.

The equilibrium amounts of pyridine sorbed by the coals are plotted against relative pressure of pyridine in Figures 2. For the Illinois No. 6 whole coal, extraction residue, and extract, the isotherms are linear or nearly linear over the relative pressure range of 0.2 to 0.8. For the whole Illinois No. 6 coal, the linear region was found to extend down to 0.05 relative pressure. Additionally, the slopes for the three materials for each coal are similar but the intercepts are quite different. The dramatic increase in intercept upon pyridine-extraction is particularly striking.

We have also determined the sorption isotherms for the three O-alkylated whole Illinois No. 6 coals. The isotherms, shown in Figure 2, are also linear over the range 0.2 to 0.6 relative pressure. The intercept decreases with the size of added alkyl group.

## DISCUSSION

### Dual-Mode Sorption.

We propose that the isotherms can be modelled in terms of a dual-mode sorption mechanism used to explain the sorptive behavior of glassy polymers. This mechanism, introduced by Meares in 1954<sup>3</sup>, and further developed by Barrer et al.<sup>4</sup>, Michaels et al.<sup>5</sup>, and Vieth<sup>6</sup>, describes the sorption mechanism in terms of one population of ordinarily dissolved sorbate which resides in the polymer matrix and is described by Henry's law (i.e. sorption is linear with pressure) while the second population of sorbate is considered to occupy unrelaxed free volume within the polymer matrix and is described by a Langmuir isotherm. This unrelaxed free volume comes about due to restricted rotations of the polymer chains in the glassy state and represents the fixed microvoid or "holes" throughout the polymer. These microvoids act to immobilize a portion of the penetrant molecules by entrapment or by binding at high energy sites at their molecular peripheries (similar to adsorption).

The equilibrium isotherm of the dual sorption model can be expressed by the following equation:

$$C = C_0 + C_H = k_D p + (C'_H b p) / (1 + b p) \quad (1)$$

where C is solubility;  $k_D$  is Henry's Law dissolution constant; b is the hole affinity constant;  $C'_H$  is the hole saturation constant, and p is the pressure. The first term,  $C_0$ , represents sorption of normally diffusible species while the second term,  $C_H$  represents sorption in microvoids or "holes." When  $b p \ll 1$ , the isotherm reduces to a linear form

$$C = [k_D + C'_H b] p \quad (2)$$

At sufficiently high pressures, the microvoids become saturated and will no longer sorb additional penetrant. When  $b p \gg 1$ , sorption in the microvoids reaches a saturation limit,  $C'_H$  and Equation 1 reduces again to a linear form:

$$C = k_D p + C'_H \quad (3)$$

Thus the dual mode sorption model predicts that a plot of C vs p will consist of a low-pressure linear region and high-pressure linear region connected by a nonlinear region.

**Coal-Pyridine Isotherms.** Equation 3 is an equation of a straight-line with a slope of  $k_d$ , the dissolution constant, and an intercept of  $C'_H$ , the hole saturation constant. For the pyridine sorption isotherms shown in Figure 2, we propose that the slopes ( $k_d$ ) are a measure of the solubility of pyridine into the coal matrix and the intercepts ( $C'_H$ ) correspond to the micropore volume available to pyridine. Support for this interpretation includes:

**Isotherm Slopes.** The amount of pyridine sorbed by the whole coal, pyridine-extract, and extraction residue increases linearly with pressure over a wide pressure range (for the whole coal.  $p/p_0$  of 0.05 to 0.8). This Henry's law behavior suggest that dissolution is the dominant process over this pressure range. Moreover, the slopes of the isotherms are very similar for the Illinois No. 6 coal, extract, and residue. Since these materials are all of the same chemical constitution by elemental analysis and NMR analysis<sup>9</sup>, similar slopes are expected if the linear portion of the isotherms represent dissolution of pyridine into the matrix.

It is possible that mesopores are being filled in this high pressure region due to capillary condensation. However, mesoporous solids often exhibit an upturn in the isotherm in the midpressure region<sup>7</sup> which is absent in our isotherms. In addition, pyridine is known to be a good swelling solvent and we can expect the coal to swell (dissolve into the solid) in this pressure region as well. The process of swelling is expected to significantly alter the pore structure of coal in this high pressure region.<sup>10</sup> The remarkable similarity of the slopes of the isotherms for all materials (whole coal, extract, and residue) is, in our opinion, best explained by a dominant process of dissolution of pyridine into the matrix.

**Isotherm Intercepts.** The steep rise in the low pressure region of the whole Illinois No. 6 coal suggests that it is micropores that are being filled, with a corresponding enhancement of the interaction potential and therefore of the enthalpy of adsorption. This enhanced interaction potential will occur at about 1.5 to 2.5 the diameter of the pyridine molecule, depending on whether the pore is slit-like or cylindrical, respectively. The maximum diameter of the pyridine molecule is about 6.8 Å. This suggests a maximum diameter of 17 Å for the diameter of the pores being filled.

The intercept of the isotherm of the Illinois No. 6 whole coal, when converted to a volume of pyridine per g of dmmf coal, agrees well with the micropore volume (< 12 Å) determined for an Illinois #6 coal (PSOC-26) by Walker and coworkers using nitrogen adsorption and mercury and helium displacement.<sup>11</sup> Our value is 0.055 mL/g compared to their value of 0.066 mL/g coal. The agreement is quite good considering that different probes are being used in each case.

**Effect of Pyridine Extraction.** The extraction residues have an intercept two to three times that of the whole coals. According to our interpretation, this is due to a dramatic increase in micropore volume upon pyridine extraction. Solvent extraction has been demonstrated to increase the micropore volume and surface areas for Wyodak subbituminous coal,<sup>12</sup> consistent with these results. The interpretation is that solvent extraction creates new micropores in the coal, thus leading to an increased intercept for the extraction residue.

**Effect of O-methylation.** Pyridine is a polar molecule capable of hydrogen bonding with the hydroxyl groups in the coal. Interaction at these hydrogen bonding sites is expected to be strong in comparison to other interaction sites in the coal and, consequently, pyridine adsorbed at low pressures may preferentially interact at these sites. Thus, one might reasonably expect that the intercepts observed are related to a hydrogen bonding effect.

We have tested this hypothesis by conducting experiments on the O-methylated coal. As seen in Figure 6, O-methylation has little or no effect on the intercept value. Pyridine cannot hydrogen bond to the O-methylated materials. If hydrogen bonding were the cause of the intercepts, the intercepts should be substantially diminished upon hydrogen bonding. That do not suggest another cause for their existence. We argue that the intercepts are related to the microporosity of the coal.

Additionally, the slope of the straight portion of the O-methylated coal is considerably less than that of the whole coal. If the slope is a measure of the solubility of pyridine in coal, then the effect of O-methylation is to reduce the pyridine solubility. This seems logical, given that the O-methylated coal cannot hydrogen bond to pyridine.

**Effect of O-alkylation.** O-alkylation of the whole Illinois No. 6 coal with bulky, alkyl groups results in a reduction of the intercept, consistent with a reduction in micropore volume as the large alkyl groups fill micropores. The intercepts for the series of O-alkylated coals correlate remarkably well with the microporosities measured by Liotta using mercury porosimetry and helium penetration.<sup>8</sup>

Finally, we argue that the micropore volume determined by this technique should be representative of the **unswollen** coal since the micropores are being filled or nearly filled at very low pressures (less than  $p/p_0$  of 0.05 for the whole coal) and swelling by pyridine at these pressures should be minimal. In addition, the micropore volume determined by this method is obtained by **extrapolation** to zero dissolution (or swelling).

#### CONCLUSIONS

Pyridine sorption isotherms for Illinois No. 6 coal give straight-line curves with nonzero intercepts. We have interpreted these lines in terms of a dual-mode model for sorption of gases by glassy polymers. We believe the several lines of evidence discussed above support our interpretation that the intercept values represent micropore volume available to pyridine. Thus, determination of pyridine sorption isotherms may be an effective technique for tracking micropore volume coals and modified coals. Further work is planned to further explore the dual-mode sorption model presented here, with specific attention paid to the low pressure isotherms of these materials.

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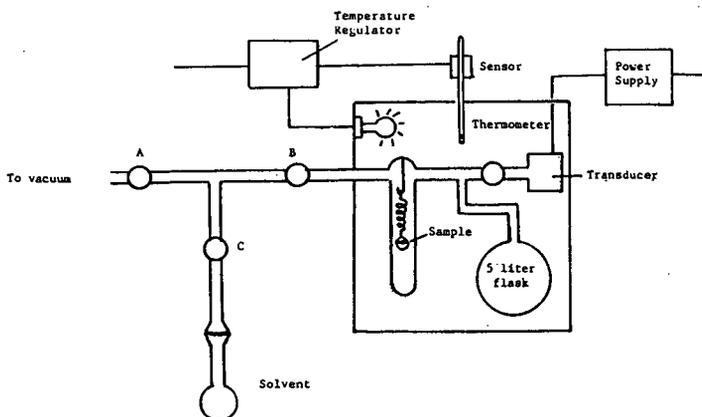


Figure 1. Sorption Apparatus

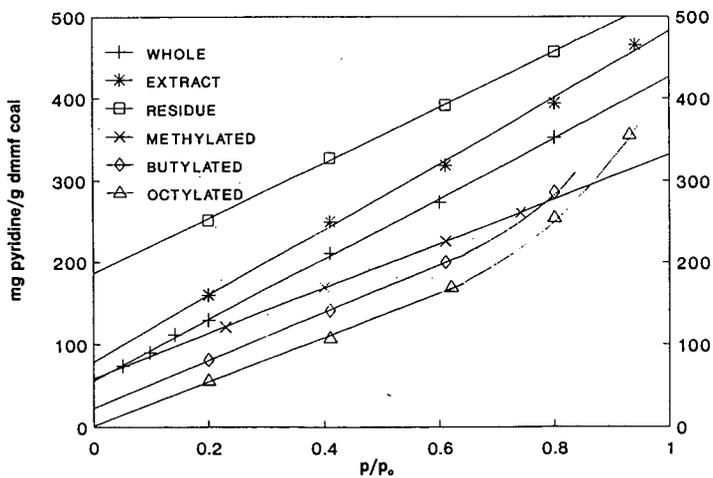


Figure 2. Sorption Isotherms for Illinois No. 6 Coals at 50°C.